Validation for control of organically bound tritium in the environment of nuclear plants

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Abstract. The objective of the research was to study migration of tritium and carbon compounds in the classic chain: radioactive waste (RW) storage facility – ground water - (coniferous trees) water reservoirs – drinking water. The method of the successive cascade filtration of water samples was used for the first time. This method allowed separating the organically bound tritium (OBT) from the tritium oxide HTO. For some samples, the chemical analyses have been carried out to identify organic substances. It was determined that all samples contained mainly OBT. The filters trap the organic substances containing 80-100% of tritium activity. The HTO contribution is less than 20%; such amount of activity passes through all filters. This is a sufficient basis to justify the necessity of the OBT monitoring at nuclear facilities. For the purpose of the OBT monitoring, the successive filtration method is to be applied with respect to samples in the environment of typical nuclear facilities and nuclear plants.

1. Introduction

Common dosimetry methods based on the HTO measurement can under-assessed significantly the OBT specific hazard, because the OBT half-life period is more than a year, while that of HTO is 10 days. Limitation of tritium should be carried out for the OBT, norms for which (according to NRB-99/2009) are 2.5 times less than for HTO.

The objective of the research was to study migration of tritium and carbon compounds in the chain: the RW storage facility – ground water - (coniferous trees) water reservoirs – drinking water. The first subtask was to identify (according to the particle size) types of organic substances migrating; the second one was to determine the amounts of tritium and carbon, C-14, contained in those substances. The third subtask was to use the obtained data in practice. The solution of these three subtasks will justify the need to control the organically bound tritium (OBT) in the environment of the nuclear facilities and nuclear plants.

As for hydrogen replacement by tritium in water molecule and migration of tritium oxide HTO (or T_2O) via water, we believe this problem is well studied. Therefore, in this work, we paid attention to another task – examination of tritium contents in organic materials. To solve this problem, about 60 samples have been collected from the special control boreholes and from the neighbor water reservoirs (the lake, swamps, streams and springs). Moreover, snow samples have been collected on the site of the RW storage facility as well as samples of pine needles on the same site. To separate tritium oxide HTO from other types of tritium containing materials, the successive two-cascade sample filtration was being carried out using the “Barrier”-type carbonic filter. Such filter retains particles more than 1 µm. In addition, the membrane reverse osmosis filter T&M 1.OOS was also used to retain Nan particles more than 0.1nm. Total number of tritium (carbon) measurements was about 200. With this purpose, we applied the successive cascade

filtration of tritium containing samples. However, the cascade filtration principle is used in medicine – for blood separation – and in hydrogeology – for separation of organic materials (B. Dupre's method [10]). Carbon-14 is an inherent component of organic materials; its presence in hydrosphere is often man-made. In our case, C-14 presence confirms the presence of organic substances. Organically bound tritium is a special case of tritium enclosed in the structure of different materials. In general, tritium can be included in O-H or N-H chains without carbon. In addition to tritium, OBT also contains carbon (in particular, C-14) and oxygen, because tritium can be present in O-H chain [1]. It is also necessary to consider the possibility of replacing hydrogen with tritium in sulphydryl (S-H) and amide compounds as well as in amino-groups (N-H). In our opinion, on a par with the term «organically bound tritium» the term «oxygenated hydrocarbon compounds containing tritium» should be used. The following compounds comply with such definition: hydrocarbons, alcohols (as low molecular organic substances), humus substances, humic acids, hydrocarbons and their derivatives, resins, phenols, aldehydes etc. [2].

Carbonic acid (and its hydrocarbon salts), some humic acids and other low molecular organic substances are retained by the membrane reverse osmosis filters because of the molecule sizes from 0.1nm [3]. The size of water molecule is assumed to be 0.095nm [4]. Complex organic macromolecules and bacteria [5, 6] are retained by the carbonic filter, because their size exceeds 1μm [1].

2. Method of research

Water samples collected in the hydrosphere media nearby the RW storage facilities were the subject of research. These samples have been collected from: the borehole under the storage facility (borehole 005); borehole upwards along the ground water movement (borehole 144); ground water exit-site to the surface: the lake (bayou), spring; in addition, the tap water has been sampled on the storage site and in the nearest city. Snow and pine needles have also been sampled. Samples were taken in 1.5 litre bottles with a tight lid.

Before each sample measuring, hydrocarbon (HCO_3^-) concentration was determined by the method [7] using titration of hydrochloric acid with addition of methyl orange, while concentration of organic substances, C_{org}, was determined by oxidation method [2] using $KMnO_4$. At that, 1mg of O_2 oxidizer corresponds to 4mg $KMnO_4$ and 21mg oxidized organics [2]. The spectrophotometer is used for permanent control C_{org} in water.

After that, the successive two-cascade sample filtration has been performed [8]. At the first stage, the carbon filter («Barrier») was used, and then the reverse osmosis filter (T&M 1.OOC) was used to measure hydrocarbon concentration, concentration of organic substances and sample activity - to separate different types of tritium. Two filters retain only HTO of less than 0.1nm molecules. According to the literature data, carbon filters retain more than 1μm particles. In fact, such filters are used to protect the polymeric, membrane, reverse osmosis filter T&M 1.OOC, retaining more than 0.1nm particles. Moreover, the carbon filter separates the complex organics with more than 1μm molecules from low molecular tritium-containing organics (acids, alcohols, hydrocarbons) with molecules from 0.1nm to 1μm. The reverse osmosis filter is used to separate low molecular tritium containing organic compounds from tritium oxide HTO. After tritium specific

sampling, the filters were rinsed with Moscow tap water up to the background. Our method of the successive filtration differs from the Dupre's method of the organic material cascade filtration [9] in the fact that for organic substances, dependences of such substance distribution on activity of tritium and carbon C-14 retained of the filters are determined additionally.

Activity measurement of tritium and C-14 using Tri-Carb 3180 analyzer. Tri-Carb 3180 is a computerized desktop liquid scintillation luminescent analyzer to find and study extremely low amounts of beta active isotopes. Minimum detectable activity (by tritium) is 1Bq/l. In Russia, the average background by tritium is 1-3Bq/l [8]. For measurement by Tri-Carb 3180, Ultima Gold LLT scintillator was used in the ratio 10ml (or 5ml) of the sample to 10ml of the scintillator. The measurement duration was at least 100min. Moscow tap water served as a background by tritium (1.5imp/min).

As for the pine needle samples, two standard methods other than those mentioned in [10] were used. According to the first method, needles were boiled during 15min, and then the decoction sample was measured using TriCarb 3180 analyzer. According to the second method, needles were infused on ethanol during three days and then measured. The tritium specific activity was determined on the basis of dried needles weight (HTO separation) and water or alcohol volume.

3. Results of measurement and analysis

According to the research method, the samples were subjected to the chemical analysis (concentration determination of hydrocarbons and organic substances).

Table 1 – Results of the chemical analysis of samples

Sample		Concentration of hydrocarbon, mg/l	Concentration of organic matter C_{org} [9], mg/l
Water from Borehole 005*	Original sample	910	16,0
	After «Barrier» filter	350	0
	After membrane filter	0	0
Water from lake Bayou*	Original sample	620	20,0
	After «Barrier» filter	150	0
	After membrane filter	0	0
Melted snow*	Original sample	610	26,0
	After «Barrier» filter	152	0
	After membrane filter	0	0
Tap water on-site	Original sample	366	10,5
	After «Barrier» filter	152	0

**Borehole 005 – The borehole under the storage facility; Bayou – the water reservoir in 500 meters from the storage facility.*

Then, according to the sample examination method, the samples were subjected to successive filtration using at the first stage the «Barrier»-type carbon filter and at the second stage using the membrane filter T&M 1.OOC. The obtained data permit to conclude that such method of purification from organically bound tritium is rather effective. Table 1

demonstrates that organics is retained by filters and the degree of retaining depends on the particle (or organic molecule) sizes.

Table 2 – Results of the sample filtration. Measurements over the energy range 0 – 12 keV (tritium)

Sample		Measurement		Tritium activity concentration in the retained organics, Bq/l
		Tritium activity concentration, Bq/l	Error , %	
Water from Borehole 005	Original sample	1450	4,7	-
	After «Barrier» filter	78,0	5,6	1372
	After membrane filter	28,1	6,4	49,9
Water from Borehole 144*	Original sample	72,8	3,9	-
	After «Barrier» filter	46,2	6,2	26,6
	After membrane filter	26,3	7,2	19,9
Water from lake Bayou	Original sample	398	6,2	-
	After «Barrier» filter	42,5	6,8	355,5
	After membrane filter	22,2	6,2	20,3
Spring on the beach	Original sample	43,7	4,0	-
	After «Barrier» filter	7,30	5,6	36,4
	After membrane filter	0,00	7,0	7,30
Tap water from the village	Original sample	24,0	6,8	-
	After «Barrier» filter	3,60	7,2	20,4
	After membrane filter	0,00	4,4	3,60
Tap water on-site	Original sample	131	6,0	-
	After «Barrier» filter	75,7	7,8	55,3
	After membrane filter	29,4	12,2	46,3
Needles after infusions on alcohol		137,4**	6,1	-
Needles after decoction		58,6***	5,7	-

**Borehole 144 – The borehole in 100 meters from the storage facility;*
*** Weight of needles ≈5g, volume of alcohol 50ml*
**** Weight of needles ≈ 9г, volume of water 200ml*

Table 3 – Percentage between OBT and HTO in samples

Sample	Quantity of OBT, %	Quantity of HTO, %
Borehole 005	98	2
Borehole 144	91	9
Bayou	94	6
Tap water from the village	100	0
Spring on the beach	100	0
Tap water on-site of 13.12.10	77	23

Table 2 demonstrates: for the sample from Borehole 005 – 94% of tritium activity delays on the «Barrier» filter; while for the sample from Borehole 144 – 37%; for a tincture of alcohol and decoction of the pine needles, as result of re-calculation, we got

approximately the same result – more than 1800 Bq/kg, in terms of which we can conclude that the pine needles accumulate OBT.

The organics retain on the filters – this fact is confirmed by the reduction of C-14 in samples (carbon-14 on a par with carbon-12 is an integral part of an organic compound). Table 4 demonstrates this fact.

Table 4 – Results of the sample filtration. Measurements over the energy range 12 – 156 keV (carbon 14)

Sample		Measurement: Activity concentration of C-14 in water, Bq/l	Measurement: Error , %	Tritium activity concentration in the retained organics, Bq/l
Water from Borehole 005	Original sample	18,4	3,7	-
	After «Barrier» filter	7,20	4,0	11,2
	After membrane filter	1,00	4,3	6,2
Water from lake Bayou	Original sample	19,6	3,0	-
	After «Barrier» filter	5,70	4,3	13,9
	After membrane filter	0,80	4,1	4,9
Melted snow	Original sample	13,4	5,1	-
	After «Barrier» filter	8,30	5,7	5,1
	After membrane filter	1,10	5,8	7,2
Tap water from the village	Original sample	18,8	5,4	-
	After «Barrier» filter	4,30	8,0	14,5
	After membrane filter	0,00	4,1	4,3
Tap water on-site	Original sample	7,40	5,7	-
	After «Barrier» filter	4,80	8,1	2,6
	After membrane filter	0,50	8,3	4,3
Needles after infusions on alcohol		90,8	6,2	-
Needles after decoction		36,6	6,5	-

Tables 2- 4 demonstrate that organics containing 80-100% of tritium (and C-14) activity are retained by the filters. This fact confirms that OBT contribution in samples is 80-100%.

Maximum amount of tritium has been found in the borehole near the RW storage facility (1500 Bq/l); according to the Russian Radiation Safety Standards, NRB - 99/2009, this is about 1/5 of the intervention level for HTO (7700 Bq/l). The obtained data show that sound tritium levels in the environment are induced by tritium leakage from the RW storage facility.

4. Conclusion

The method of successive filtration of tritium containing water samples has been applied. This method promotes separation of organically bound tritium (OBT) from tritium oxide (HTO). It has been revealed that all samples contain mainly OBT (the filters retain organics containing 80-100% of tritium activity), the HTO contribution is less than 20%. This fact assumes to be sufficient to justify the necessity of the OBT control at nuclear

facilities. Further studies are to be continued at other nuclear facilities and nuclear plants in order to examine the OBT contents in the environmental media.

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